

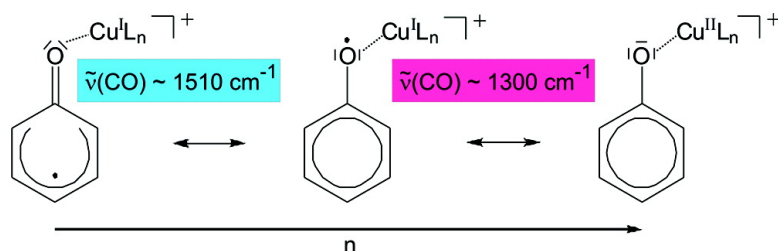
Communication

The C#O Stretch as an Unprecedentedly Large Spectral Marker for the Electron Transfer between Copper(II) and a Phenolate Anion

Petr Milko, Jana Roithova#, Nikos Tsierkezos, and Detlef Schro#der

J. Am. Chem. Soc., **2008**, 130 (23), 7186-7187 • DOI: 10.1021/ja801079r • Publication Date (Web): 14 May 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

The C–O Stretch as an Unprecedentedly Large Spectral Marker for the Electron Transfer between Copper(II) and a Phenolate Anion

Petr Milko,[†] Jana Roithová,^{*,†,‡} Nikos Tsierkezos,[†] and Detlef Schröder[†]

Faculty of Science, Department of Organic Chemistry, Charles University in Prague, Hlavova 8, 12843 Prague 2, Czech Republic, and Institute of Organic Chemistry and Biochemistry, Flemingovo nám. 2, 16610 Prague 6, Czech Republic

Received February 12, 2008; E-mail: roithova@natur.cuni.cz

Copper ions bound to nitrogen and oxygen ligands are a central motif in many copper-containing redox enzymes. The arrangement of ligands around the metal strongly depends on the oxidation state of copper and therefore also can substantially determine the reactivity of the active site.^{1–3} The influence of the coordination sphere on the properties and reactivity of copper ions is extensively discussed in the literature using models of copper ions solvated by water^{4,5} or ammonia.⁶ It has been shown that Cu^I prefers coordination of two ligands only, whereas Cu^{II} usually accepts four to six ligands.^{4,7} Here, we show the influence of the coordination sphere on the bonding between copper(II) and a phenolate anion (PhO[−]), a unit playing a role in redox enzymes such as galactose oxidase,^{8–10} using infrared multiphoton dissociation (IRMPD) experiments and density functional theory (DFT).

In the bare [Cu(PhO)]⁺ cation,¹¹ the bonding between Cu^{II} and PhO[−] is associated with electron transfer where copper is reduced to Cu^I and bound to a phenoxy ligand. The effect of additional ligands on the structure of the copper/phenoxy core is investigated first by B3LYP/TZVP calculations. In addition to the simplest ligands, ammonia and water, also pyridine as an aromatic nitrogen ligand and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) as a bidentate ligand is considered. Coordination of one monodentate ligand to [Cu(PhO)]⁺ has only a small effect on the structure and the spin distribution of the core (Table 1). The arrangement of ligands is linear, and the length of the bond between copper and the oxygen atom of the phenoxy ligand slightly decreases upon attachment of a ligand due to the effect of the more pronounced *sd*- σ hybridization.¹² Coordination of further monodentate ligands leads to an elongation of the Cu–O bond, which can be understood as a result of the interplay between the steric demands of the ligands and the increasing electrostatic attraction between copper and the phenoxy ligand, of which the former prevails. The analogous trend is also found for the carbon–oxygen bond of the phenoxy ligand, which shortens upon the coordination of the first additional ligand to [Cu(PhO)]⁺, whereas further ligands induce a slight elongation. All values found for the bidentate ligand TMEDA are consistent with the view that TMEDA has an analogous effect like two monodentate ligands, except a shortening of the Cu–O bond in the [Cu(PhO)]⁺ core. The latter effect can be attributed to the lower steric demands of TMEDA in comparison to two monodentate ligands (the O–Cu–N angle in [Cu(PhO)(TMEDA)]⁺ is 135.6° compared to 120.5° for [Cu(PhO)(NH₃)₂]⁺).

Three selected complexes, [Cu(PhO)(H₂O)]⁺, [Cu(PhO)(Py)]⁺ (Py = pyridine), and [Cu(PhO)(TMEDA)]⁺, are further characterized by IRMPD of the mass-selected ions (for details about fragments and bands, see Supporting Information).^{11,13} The IRMPD

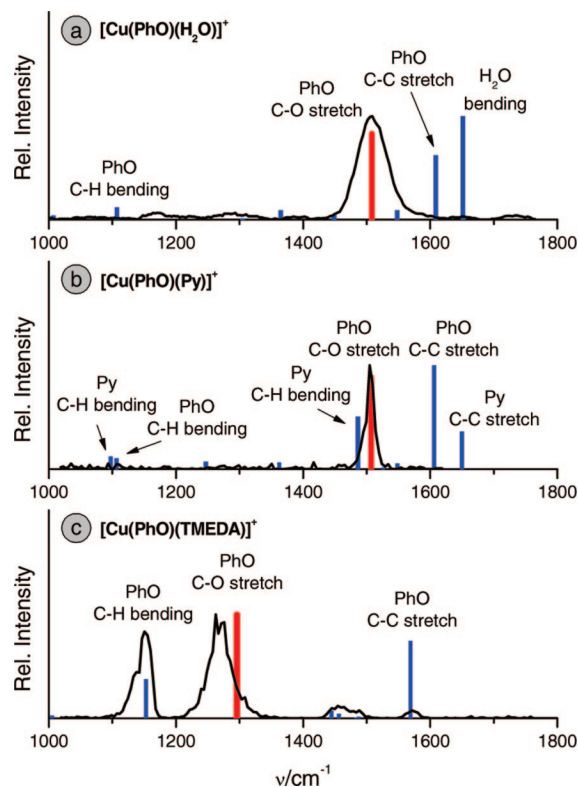


Figure 1. Experimental IRMPD and computed IR spectra of [Cu(PhO)(H₂O)]⁺ (a), [Cu(PhO)(Py)]⁺ (b), and [Cu(PhO)(TMEDA)]⁺ (c).

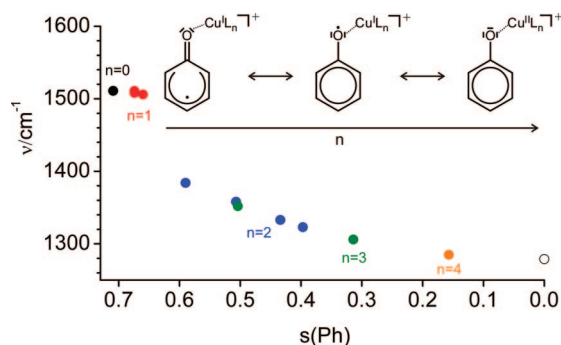


Figure 2. Mesomeric structures of [Cu(PhO)]⁺ and the dependence of $\nu(\text{C–O})$ on the calculated spin density of the phenyl ring. The open symbol corresponds to the calculated value of free phenol.

[†] Institute of Organic Chemistry and Biochemistry.

[‡] Charles University in Prague.

spectra of the complexes with water or pyridine as additional ligands are dominated by bands corresponding to the C–O stretch (1508

Table 1. Theoretical Parameters for [Cu(PhO)(L)_n]⁺ Complexes with L = NH₃, H₂O, Pyridine, and TMEDA for n = 1–4^a

L	n	bond length [Å]		s (X) ^b			q (X) ^d			Cu bonding orbital ^e	ν(CO) ^f [cm ⁻¹]	bond energy [eV] Cu–OPh
		Cu–O	C–O	X = Cu	X = O	X = Ph ^c	X = Cu	X = PhO	X = (L) _n			
NH ₃	0	1.877	1.279	0.010	0.281	0.709	0.68	0.32		93/4	1511	2.60
	1	1.858	1.277	0.027	0.300	0.674	0.44	0.27	0.29	90/10	1511	2.36
	2	1.902	1.286	0.146	0.322	0.507	0.51	0.07	0.42	97/3	1358	0.74
	3	1.934	1.308	0.339	0.284	0.314	0.56	−0.12	0.56	99/1	1306	0.66
H ₂ O	4	1.976	1.328	0.490	0.222	0.157	0.61	−0.31	0.70	99/1	1285	0.62
	1	1.850	1.278	0.028	0.297	0.674	0.55	0.27	0.18	91/9	1508	2.45
	2	1.864	1.282	0.086	0.317	0.590	0.59	0.17	0.24	95/5	1384	1.20
pyridine	3	1.868	1.290	0.163	0.321	0.504	0.62	0.08	0.30	97/3	1352	1.04
	1	1.859	1.277	0.034	0.306	0.660	0.43	0.25	0.32	90/10	1506	2.23
TMEDA	2	1.875	1.294	0.206	0.313	0.434	0.48	0.01	0.51	97/3	1333	0.61
	2	1.834	1.301	0.221	0.294	0.397	0.48	−0.02	0.54	96/4	1323	1.72

^a Computational details and optimized geometries can be found in the Supporting Information. ^b Spin densities determined by Mulliken population analysis. ^c Sum of spin densities for all atoms of the phenyl ring of the phenoxy ligand. ^d Charge densities determined by Mulliken population analysis. ^e Contributions of the 4s and 3d orbitals to the bonding orbital on Cu determined by natural bond orbital analysis. ^f Harmonic frequencies, not scaled.

and 1504 cm⁻¹, respectively) with frequencies typical for free phenoxy radicals (Figure 1).¹⁴

The IRMPD spectrum obtained for [Cu(PhO)(TMEDA)]⁺ is strikingly different in that the C–O stretch is drastically red-shifted to 1269 cm⁻¹, which is close to the frequencies usually found for C–O single bonds.¹⁵ Inspection of the computed spectra of the other complexes (Table 1) shows a systematic trend. Thus, the C–O stretching vibration for [Cu(PhO)L_n]⁺ with n = 0 or 1 is in the range of 1510 cm⁻¹, whereas the corresponding C–O modes are shifted to lower values of about 1300 cm⁻¹ for the [Cu(PhO)L_n]⁺ complexes with n > 1.¹⁶

The rationale for the pronounced stepwise red shift can be found in the effect of the ligand field on the electronic distribution in the [Cu(PhO)]⁺ core. Thus, the electron distributions in free [Cu(PhO)]⁺ and the monoligated [Cu(PhO)L]⁺ complexes show that the spin density is delocalized over the aromatic moiety of the phenoxy ligand (Table 1). In contrast, coordination of two ligands to [Cu(PhO)]⁺ results in a transfer of spin density from the aromatic ring to the oxygen atom of the phenoxy ligand and copper, which becomes even more pronounced upon coordination of a third and fourth ligand (Figure 2). In the latter case, the unpaired electron is by and large shared between oxygen and copper, while the aromatic ring retains six π-electrons. The changes in electron distribution have an immediate effect on the bond order of the C–O bond as revealed by the corresponding IR frequencies.

Interestingly, synthetic models of the active center of enzyme galactose oxidase (GAO) contain a core of copper(II) bound to phenolate with additional coordination by four ligands (analogous to the systems studied here).¹⁷ The C–O stretching mode of these model systems thus appears at about 1300 cm⁻¹. Electrochemical oxidation of such a complex leading to a copper(II)/phenoxy core (not studied here) shifts the C–O vibration to about 1510 cm⁻¹, reflecting the creation of the radical site in the aromatic ring.^{18,19}

In summary, coordination of more than one N or O donor ligand to the copper(I)/phenoxy complex results in a shift of the radical site from the aromatic moiety to the oxygen and copper atoms and hence a formal isomerization to the Cu(II)/phenolate complex. The change in the spin distribution occurs in a stepwise manner from two- to three-fold coordination and is revealed by an unprecedentedly large red shift of the corresponding C–O frequency by more than 200 cm⁻¹.

Acknowledgment. Dedicated to Prof. Helmut Schwarz on the occasion of his 65th birthday. The authors thank the Grant Agency of the Academy of Sciences of the Czech Republic (KJB400550704), the Ministry of Education of the Czech Republic (MSM0021620857), and the Academy of Sciences of the Czech Republic (Z40550506) for support, and Dr. Joel Lemaire for help during the measurements at the CLIO facility.

Supporting Information Available: Experimental and computational details, optimized geometries, and energies at 0 K of all calculated complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (a) Basumallick, L.; Szilagy, R. K.; Zhao, Y. W.; Shapleigh, J. P.; Scholes, C. P.; Solomon, E. I. *J. Am. Chem. Soc.* **2003**, *125*, 14784. (b) Basumallick, L.; Sarangi, R.; George, S. D.; Elmore, B.; Hooper, A. B.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **2005**, *127*, 3531.
- Raffa, D. F.; Rickard, G. A.; Rauk, A. *J. Biol. Inorg. Chem.* **2007**, *12*, 147.
- Kandori, H.; Nakamura, H.; Yamazaki, Y.; Mogi, T. *J. Biol. Chem.* **2005**, *280*, 32821.
- Pasquarello, A.; Petri, I.; Salmon, P. S.; Parisel, O.; Car, R.; Tóth, É.; Powell, D. H.; Fischer, H. E.; Helm, L.; Merbach, A. E. *Science* **2001**, *291*, 856.
- Chaboy, J.; Munoz-Paez, A.; Merkl, P. J.; Marcos, E. S. *J. Chem. Phys.* **2006**, *124*, 064509.
- Inoue, K.; Ohashi, K.; Iino, T.; Judai, K.; Nishi, N.; Sekiya, H. *Phys. Chem. Chem. Phys.* **2007**, *9*, 4793.
- Blumberger, J.; Bernasconi, L.; Tavernelli, I.; Vuilleumier, R.; Sprik, M. *J. Am. Chem. Soc.* **2004**, *126*, 3928.
- Whittaker, J. W. *Chem. Rev.* **2003**, *274*, 2347.
- Thomas, F. *Eur. J. Inorg. Chem.* **2007**, 2379.
- Rokhsana, D.; Dooley, D. M.; Szilagy, R. K. *J. Am. Chem. Soc.* **2006**, *128*, 15550.
- Milko, P.; Roithová, J.; Schröder, D.; Lemaire, J.; Schwarz, H.; Holthausen, M. *Chem.—Eur. J.* **2008**, *14*, 4318.
- Bauschlicher, C. W.; Langhoff, S. R.; Partridge, H. J. *Chem. Phys.* **1991**, *94*, 2068.
- (a) Dopfer, O. *J. Phys. Org. Chem.* **2006**, *19*, 540. (b) Polfer, N. C.; Oomens, J. *Phys. Chem. Chem. Phys.* **2006**, *9*, 3804. (c) MacAleese, L.; Maitre, P. *Mass Spectrom. Rev.* **2007**, *26*, 583.
- Schnepf, R.; Sokolowski, A.; Müller, J.; Bachler, V.; Wiegardt, K.; Hildebrandt, P. *J. Am. Chem. Soc.* **1998**, *120*, 2352.
- In the comparison of measured IRMPD and computed IR spectra, the positions of the bands are much more significant than intensities; see: Schröder, D.; Schwarz, H.; Milko, P.; Roithová, J. *J. Phys. Chem. A* **2006**, *110*, 8346.
- Note that TMEDA is bidentate ligand and corresponds formally to n = 2.
- Sokolowski, A.; Leutbecher, H.; Weyhermüller, T.; Schnepf, R.; Bothe, E.; Bill, E.; Hildebrandt, P.; Wiegardt, K. *J. Biol. Inorg. Chem.* **1997**, *2*, 444.
- Whittaker, J. W. *Arch. Biochem. Biophys.* **2005**, *433*, 227.
- Nagano, Y.; Liu, J.-G.; Naruta, Y.; Ikoma, T.; Tero-Kubota, S.; Kitagawa, T. *J. Am. Chem. Soc.* **2006**, *128*, 14560.

JA801079R